Data Validation SOP

HW-25, Rev. 2

Dioxin/Furans

SOP NO. 25
REVISION 2
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USEPA REGION II DATA VALIDATION SOP FOR EPA METHOD 1613, REVISION A
Tetra- through Octa-chlorinated Dioxins and Furans by Isotope Dilution (HRGC/HRMS)

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Optional Quality Control and Assurance Requirements for Validation

1.0 INTRODUCTION

This method is designed to meet the survey requirement of the USEPA ITD. The method is used to detect the Tetra- through octa- chlorinated dibenzo-p-dioxins and dibenzofurans associated with the Clean Water Act (CWA, as amended 1987); the Resource Conservation and Recovery Act (RECRA, as amended 1986) and the Compensation and Liability Act (as amended in 1986) and other dioxins and furan compounds amenable to this method.

The dioxins and furans may be determined in waters, soils, sludges and other matrices using this method. The method is based on EPA, industry, and academic methods.

2.0 APPLICABILITY

The attached Standard Operating Procedure (SOP) is applicable to polychlorinated dibenzodioxin and polychlorinated dibenzofuran (PCDD/PCDF) data obtained using EPA Method 1613A, Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by Isotope Dilution using High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), April 1990. Its scope is to facilitate the data validation process of the data reported by the contracting laboratory and to ensure that the data is being reviewed in a uniform manner. This SOP is based upon the quality control and quality assurance requirements specified in Method 1613A, April 1990.

3.0 Responsibilities/Scope

3.1 The reviewer must be knowledgeable of the analytical method and its QC Criteria.

3.2 The reviewer must complete the following:

3.2.1 Data Assessment Checklist - The data reviewer must read each item carefully and must check yes if there is compliance, no if there is non compliance and N/A if the question is not applicable to the data.

3.2.2 Data Assessment Narrative - The data reviewer must present professional judgement and must express concerns and comments on the validity of the overall data package. The reviewer must explain the reasons for rejecting and/or qualifying the data. Example of Data Assessment format is provided in Attachment A.

3.2.3 Rejection Summary Form - The reviewer must submit the completed form using a ratio format. The numerator indicates the number of dioxins/furans data rejected; the denominator indicates the number of dioxins/furans fractions containing rejected compounds. Example of Data Rejection Form is provided in Attachment B.

3.2.4 Telephone Record Log - All Laboratory phone conversations must be documented on the Telephone Record Log Sheet. A photocopy of the Telephone Record Log is attached to the Data Assessment package.

3.2.5 Paperwork - Upon completion of the review the following are to be maintained with the data package and returned to the authorized person :

a. completed data assessment checklist and narrative (original)
b. Two copies of the data assessment narrative (attach copies of the Rejection Summary Form at end)
c. Telephone record Log (original and copy)
d. Rejection Summary Form (original)

3.3 Rejection of Data - All values determined to be unacceptable on the Dioxin/Furan Analysis Data Sheet (Form I) must be flagged with an "R". The qualifier R means that due to significant QA/QC problems the analysis is invalid and it provides no information as to whether the compound is present or not. Once the data are flagged with R any further review or consideration is unnecessary. The qualifier "J" is used to indicate that due to QA/QC problems the results are considered to be estimated. The qualifier "NJ" indicates that there is presumptive evidence for the presence of the compound at an estimated value.

The data reviewer must explain in the data assessment narrative why the data was qualified. He or she must also indicate all items of contract non-compliance. When 2,3,7,8- substituted TCDD, TCDF, PeCDD and PeCDF data are rejected (flagged "R") or qualified "J" the project officer must be notified promptly. If holding times have not been exceeded reanalysis of the affected samples may be requested. All qualifications and corrections on the Analysis Data Sheet must be made in red pencil.

4.0 Definitions

CALIBRATION SOLUTION: solutions containing known amounts of selected analytes, internal standards and recovery standards that are analyzed prior to sample analysis. The solutions are used to determine the ratio of the instrument response of the analytes to that of the appropriate internal standard and the internal standards to that of the recovery standards.

CALIBRATION VERIFICATION (VER): a mixture of known amounts of analytes that is analyzed every 12 hours to demonstrate continued acceptable GC/MS performance and establish the retention time window for each homologue.

CLEAN-UP STANDARD: only one labeled analyte (2,3,7,8-TCDD) is added to all samples extracts prior to any Clean-up procedure. This standard is used to differentiate between losses of analytes or internal standards during extraction and losses that occur during the various Clean-up procedures.

CONGENER: elements of the same group in the periodic table.

DEFLECTIONS: bend or broadening of a peak

ESTIMATED DETECTION LIMIT (EDL): the concentration of a analyte required to produce a signal with peak height of at least 2.5 times the background signal level. The EDL is calculated for each 2,3,7,8 substituted isomer for which the response of the quantitation and confirmation ions is less than 2.5 times the background level.

ESTIMATED MAXIMUM POSSIBLE CONCENTRATION (EMPC): the concentration of a given analyte that would produce a signal with a given area peak. The EMPC is calculated for each 2,3,7,8 substituted isomer for which the response of the quantitation and/or confirmation ions has signal to noise in excess of 2.5 times the background level but does not meet identification criteria.

FIELD CHAIN OF CUSTODY: see Traffic Report

GEL PERMEATION CHROMATOGRAPHY (GPC): removes many high molecular weight interferences that cause GC column performance to degrade. It may be used for all soil and sediment extracts and may be used for water extracts that are expected to contain high molecular weight organic compounds.

HOMOLOGUE: a member or members of a particular homologous series that has the same molecular weight but not necessarily the same structural arrangement. For example, the 28 pentachlorinated dibenzofurans are homologues.

HRGC/HRMS: high resolution gas chromatography/ high resolution mass spectrometry.

HPLC: high performance liquid chromatography

INITIAL CALIBRATION STANDARD SOLUTION (CS1-CS5): analysis of analytical standards for a series of different specified concentrations. The initial calibration is used to define the linearity and dynamic range of the response of the mass spectrometer to the target compounds.

INITIAL PRECISION AND RECOVERY (IPR): must be performed by the laboratory to establish the ability to generate acceptable precision and accuracy. The recoveries of the labeled analytes must be within 25 to 150 % recovery. The standard deviation (s) of the concentration and the average concentration (x) for each unlabeled analyte must be within range established by the Method (Table 7).

INTEGRATED ION CURRENT: electronic output to computer from instrument to provide a hard copy of area and height of a peak that

may or may not be an analyte of interest.

INTERNAL STANDARDS (IS): labeled analytes are added to every sample and are present at the same concentration in every blank, quality control sample, and calibration solution. The IS are added to the sample before extraction and are used to measure the concentration of the analytes. In Method 1613A, the ISs are $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD.

ION ABUNDANCE RATIO: mathematical comparison of selected pair of ions stipulated by the method for each target analyte. The ratio between each pair of ions must fall within established limits. These ions are needed for the identification and quantitation of target analytes.

ISOMER: chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example 1,2,3,4-TCDD and 2,3,7,8-TCDD are structural isomers.

LABELED ANALYTE (or analog): an analyte that has isotopically carbon added to its chemical structure. These compounds are used to established identification (retention time) and used for quantitation of unlabeled analytes.

MASS/CHARGE: usually expressed as m/z.

METHOD BLANK (MB): an analytical control consisting of all reagents, internal standards and surrogate standards that is carried through the entire analytical procedure. The MB is used to define the level of laboratory background contamination.

MAXIMUM CONCENTRATION LEVEL (MCL): Highest level of concentration for each analyte depending upon upper concentration of analyte. Usually used to determine upper level of the concentration range.

NON-CONGENER: elements not from the same group in the periodic table.

NON-2,3,7,8 SUBSTITUTED ANALYTES: analytes whose structure have positions other than 2,3,7,8.

ONGOING PRECISION AND RECOVERY (OPR): must be performed by the laboratory to establish the ability to maintain on a continuous basis, acceptable precision and accuracy. The recoveries of the labeled analytes must be within 25 to 150 % recovery. The standard deviation (s) of the concentration and the average concentration (x) for each unlabeled analyte must be within range established by the Method (Table 7).

PERCENT MOISTURE: an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105 °C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at this degree including water. %M is determined from decanted samples and from samples that are not decanted.

PERCENT VALLEY: see Resolution

PERFLUOROKEROSENE (PFK): compound used to establish mass spectral instrument performance for dioxin/furan analysis.

PERFORMANCE EVALUATION MIXTURE (PEM): See Performance Evaluation (PE) Sample,

PERFORMANCE EVALUATION (PE) SAMPLE: a chemical waste, soil or water sample containing known amounts of unlabeled PCDDs/PCDFs used for Quality Assurance programs. There are 3 types of PE's available. PEM Blank which consists of uncontaminated soil and used to monitor possible crossover contamination of samples in the field and laboratory. PEM Interference Fortified Blank which is a soil containing matrix interference and spiked by the laboratory with target compounds. A PEM sample(s) is a soil sample containing known amounts of unlabeled TCDD or a mixture of TCDD and other PCDD/PCDF isomers. These PEMs are used to monitor the laboratory's performance.

POLYCHLORINATED DIBENZO-P-DIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs): compounds that contain from one to eight chlorine atoms.

PCDPE: Polychlorinated Diphenylether: isomers having the same SICP and ion ratios identical to furan isomers and are monitored for interference in furan qualitative and quantitative analysis.

PRECISION AND RECOVERY (PAR) Standard: this is a stock solution containing unlabeled analytes and diluted to prepare spiking solution used for Initial Precision and Recovery (IPR) and Ongoing Precision and Recovery (OPR). This Quality Assurance program must be performed by the laboratory to establish the ability to generate acceptable precision and accuracy. The recoveries of the labeled analytes must be within 25 to 150 % recovery. The standard deviation (s) of the concentration and the average concentration (x) for each unlabeled analyte must be within range established by the Method (Table 7).

RECOVERY: a determination of the accuracy of the analytical procedure made by comparing measured values from a fortified (spiked) sample against the known spiked values. Recovery is determined by the following equation:

$$\% \text{ Recovery} = \frac{\text{measured value}}{\text{known value}} \times 100\%$$

RELATIVE RETENTION TIME (RRT): ratio of the retention time of the analyte versus the retention time of the corresponding internal standard. RRT for each analyte must be within range established by the method.

RELATIVE RESPONSE (RR): the ratio of the area response of the mass spectrometer to a known amount of an analyte (unlabeled to labeled) versus a known concentration in standard solution, plotted using linear regression. The RR is used to determine instrument performance and is used in the quantitation calculations. RR are calculated using the following equation:

$$RR = \frac{(A_n^1 + A_n^2)\, C_l}{(A_l^1 + A_l^2)\, C_n}$$

$A_n^1 + A_n^2$ are the areas of the primary and secondary m/z's for the unlabeled compound.

$A_l^1 + A_l^2$ are the areas of the primary and secondary m/z's for the labeled compound.

C_l is the concentration of the labeled compound in the calibration standard.

C_n is the concentration of the unlabeled compound in the calibration standard.

RESPONSE FACTOR (RF): the ratio of the response of the mass spectrometer to a known amount of an analyte relative to that of a known amount of internal standard as measured in the initial and continuing calibrations. The RF is used to determine instrument performance using correlation coefficient and is used in the quantitation calculations. RF are calculated using the following equation:

$$RF = \frac{(A_s^1 + A_s^2)\, C_{is}}{(A_{is}^1 + A_{is}^2)\, C_s}$$

$A_s^1 + A_s^2$	are the areas of the primary and secondary m/z's for the compound to be calibrated.
$A_{is}^1 + A_{is}^2$	are the areas of the primary and secondary m/z's for the internal standard.
C_s	is the concentration of the compound in the calibration standard.
C_{is}	is the concentration of the internal standard.

RESOLUTION: the separation between peaks on a chromatogram. Resolution is calculated by dividing the height of the valley between the peaks by the peak height of the smaller peak being resolved, multiplied by 100.

RINSATE: a portion of the solvent that is used to rinse sampling equipment. The rinsate is later analyzed to demonstrate that samples were not contaminated during collection.

SAMPLE DELIVERY GROUP (SDG): a unit within a single case that is used to identify a group of samples for delivery. A SDG is a group of 20 or fewer samples within a case, received over a period of time up to 14 calendar days. Data from all samples in a SDG are due concurrently. A SDG is defined by one of the following, whichever occurs first:

- Case; or
- each 20 samples within a case; or
- each 14 day calendar period during which samples in a case are received, beginning with receipt of the first sample in the case or SDG.

SELECTED ION MONITORING (SIM): a mass spectrometric technique whereby ions with predetermined mass/charge ratios (m/z) are monitored, as opposed to scanning MS procedures in which all m/z's between two limits are monitored.

SICP: a plot of ion abundance versus time for each ion which provides the retention time, peak area and height. This information is used for identification and quantitation of target analyte.

SIGNAL TO NOISE (S/N) RATIO: the ratio of analyte signal to random background signal. To determine the ratio, display each characteristic ion using a window 100 scans wide, and draw a base line from the lowest point in the 100 scan window. The noise is defined as the height of the largest signal (excluding signal due to PCDDs/PCDFs or other chemicals) within the 100 scan window. The signal is defined as the height of the PCDD/PCDF peak. If the data system determines the ratio, the Contractor shall demonstrate comparability between the above criteria and the automated S/N determination. Chemical noise is left to the judgement of the analyst.

2,3,7,8 SUBSTITUTED ANALYTES: analytes whose structure has other positions as well as the 2,3,7,8 positions.

TOXICITY EQUIVALENCY FACTOR (TEF): a method of converting concentrations of PCDDs/PCDFs to an equivalent concentration of 2,3,7,8-TCDD to obtain an estimation of the toxicity of the entire sample. The concentrations can be found on Form I PCDD-2 in the DFLM01.1 Statement of Work for Dioxin Analysis.

TRAFFIC REPORT (TR): (may also be called Field Chain of Custody), a sample identification form filled out by the sampler, which accompanies the sample during shipment to the laboratory and documents sample condition and receipt by the laboratory.

TWELVE HOUR TIME PERIOD: the 12 hour time period begins with the injection of the CC3 solution on the DB-5 (or equivalent) column or the injection of the column performance solution on the SP-2331 (or equivalent) column. The 12 hour period continues until 12:00 hours have elapsed according to the system clock. To be included in a given 12-hour time period, a sample or standard must be

injected with 12:00 hours of the CC3 solution or the column performance solution.

UNLABEL ANALYTE: target compound that has not been isotopically altered.

VALIDATED TIME OF SAMPLE RECEIPT (VTSR): the date on which a sample is received at the Contractor's facility, as recorded on the shipper's delivery receipt and sample traffic report.

WINDOW DEFINING MIXTURE (WDM): a mixture containing the first and last eluting isomer for each congener. The retention time for each first and last eluting isomer establishes the retention time window for each congener. All analytes in the standards (calibrations, internal standards, recovery standards, Clean-up standard) and identified analytes in samples must have a reported retention time within the established window. It is analyzed before any calibration standard, at the beginning of each 12 hour time period or when there is a shift greater than 10 seconds between retention time of recovery standards in standards or any analysis from retention time in recent calibration verification.

N/A

YES NO

PACKAGE COMPLETENESS AND DELIVERABLES

CASE NUMBER:_____
LAB:_____
SITE:_____

1.0 Data Completeness and Deliverables

1.1 Does the Traffic Report or Field Chain of Custody list all samples? [ ] ___ ___

1.2 Is the Case Narrative present? [ ] ___ ___

1.3 Are the Case Number and SDG numbers contained in the case narrative? [ ] ___ ___

1.4 Do the Traffic Reports, Field Chain of Custody or Lab Case Narrative indicate problems with sample receipt, sample condition, analytical problems, or other comments affecting the quality of the data? ___ [ ] ___

ACTION: Use professional judgement to evaluate the effect of the noted problems on the quality of the data.

2.0 Reporting Requirements and Deliverables

2.1 All deliverables must be clearly labeled with the Case number and the associated sample/traffic number. Missing or illegible or incorrectly labeled items must be identified. The Project Officer must immediately be contacted and requested to ask laboratory to submit the missing or incorrect items.

2.2 The following forms were taken from the CLP SOW, DFLM01.1 and should be specified in the Project Plan. Laboratories will not always use the exact CLP format for the forms. A comparison of CLP forms must be made against the Laboratory's version. Some information may not be found on the exact form as the CLP version but may be located on another form. As long as the information is present and accessible, it is not a problem. Are these forms (CLP or lab's version) present?

a. Sample Data Summary (Form I PCDD-1) [ ] ___
___

b. PCDD/PCDF Toxicity Equivalency Factor (Form I, PCDD-2) [ ] ___ ___

c. Second Column Confirmation Summary (Form I, PCDD-3) [ ] ___
___

d. Total Homologue Concentration Summary (Form II PCDD) [ ] ___ ___

e. PCDD/PCDF Spiked Sample Summary (Form III PCDD-1) [ ] ___
___

f. PCDD/PCDF Duplicate Sample Summary (Form III PCDD-2) [ ] ___ ___

		YES	NO	N/A
g.	PCDD/PCDF Method Blank Summary (Form IV-PCDD)	[ ]		
h.	PCDD/PCDF Window Defining Mix Summary (Form V-PCDD-1)	[ ]		
I.	Chromatographic Resolution Summary (Form V PCDD-2)	[ ]		
j.	PCDD/PCDF Analytical Sequence Summary (Form V PCDD-3)	[ ]		
k.	Initial Calibration (Form VI, PCDD-1, PCDD-2)	[ ]		
l.	Continuing Calibration (Form VII, PCDD-1, Form VII, PCDD-2)	[ ]		

ACTION: If forms are missing, contact the Project Officer to confirm which forms if any were specified in the Project Plan. If the forms are required, inform the Project Officer or obtain written permission to contact the lab for explanation/resubmittal. If the lab cannot provide missing deliverables, assess the effect on the validity of the data. Note in the Data Assessment.

2.3 GC/MS Displays
Are the following GC/MS displays present?

		YES	NO	N/A
a.	Standard and sample SIM chromatograms. SIM and TIC chromatograms must list date and time of analysis; the file name; sample number; and instrument I.D. number	[ ]		
b.	Percent peak resolution valley	[ ]		
c.	Window Defining Mixture raw data	[ ]		
d.	SIM mass chromatograms must display quantitation ion, confirmation ion, and polychlorinated diphenylether ion, where applicable.	[ ]		
e.	Integrated area and peak height must be listed for all peaks 2.5 times above background	[ ]		

ACTION: If deliverables are missing, contact the Project Officer to request explanation/resubmittals or obtain written permission to contact the lab for explanation/resubmittal. If the lab cannot provide missing deliverables, assess the effect on the validity of the data. Note in the Data Assessment.

2.4 Are the following Chain of Custody Records and in-house Laboratory Control Documents present?

		YES	NO	N/A
a.	Chain of Custody Records	[ ]		
b.	Sample Shipment Records	[ ]		
c.	Sample log-in sheets	[ ]		
d.	GC/MS Standard and Sample Run Log in chronological order	[ ]		

N/A YES NO

e. Sample Extraction Log [ ] ___ ___

ACTION: If deliverables are missing, contact the Project Officer to request explanation/resubmittals or obtain written permission to contact the lab for explanation/resubmittal. If the lab cannot provide missing deliverables, assess the effect on the validity of the data. Note in the Data Assessment.

2.5 Was the sample data package paginated and one sided? [ ] ___ ___

ACTION: If no, document difficulties of reviewing data caused by lack of pagination in Data Assessment.

3.0 Holding Times

3.1 Have any of the following holding times been exceeded?

a. For aqueous samples, 30 days from sample collection to extraction [ ] ___ ___

b. For soil/sediment samples, 30 days from sample collection to extraction [ ] ___ ___

c. For all samples 40 days from time of extraction to time of analysis [ ] ___ ___

ACTION: If holding times are exceeded, flag all data as estimated ("J"). Holding time criteria do not apply to PE samples.

Note: All samples must be stored in dark at 4 °C.

Note: **Extraction** holding times listed are recommendations. PCDDs and PCDFs are very stable in a variety of matrices. Holding times may be as high as a year for certain matrices. Sample extracts must be analyzed within 40 days of extraction.

4.0 Instrument Performance

4.1 Mass Calibration - Mass calibration of the MS must be performed prior to analyzing calibration solutions, blanks, samples, and QC samples. A static resolving power of at least 10,000 (10% valley definition) must be demonstrated at appropriate masses before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each 12 hour period of operation. Include in the narrative, minimum required resolving power of 10000 was obtained for perfluorokerosene (PFK) ion 380.9760. This is done by first measuring peak width at 5% of the maximum. This should not exceed 100 ppm, i.e., it should not exceed 0.038, for ion 380.9760. Resolving power, then is calculated using the formula,

Resolving Power = $m/\Delta m$ = 380.9760/0.038 = 10025.

NOTE: The mass calibration is generally not reported. Improper mass calibration may be detected by examining ion abundance ratios for initial and continuing calibration standards. If the mass calibration is not properly performed, the standards will not have ion abundance ratios within criteria.

N/A

YES NO

4.2 Window Defining Mixture/ Isomer Specificity Test Standards

The Window Defining Mixture must contain the first and the last isomers of each homologue PCDD/PCDF, (the labeled and internal standards are optional). The solution also should contain a series of other TCDD analytes for the purpose of documenting the chromatographic resolution.

4.2.1 For analyses on a DB-5 (or equivalent) GC column, the chromatographic resolution is evaluated by the analysis of Isomer Specificity Test Standards at the beginning of every 12 hour period. Was this performed accordingly? [___] ___ ___

ACTION: If the Isomer Specificity Test Standards was not analyzed at the required frequency, use professional judgement to determine the effect on the quality of the data. Document in Data Assessment under contract non-compliance.

4.2.2 Were all peaks labeled and identified on the Selected Ion Current Profiles (SICPs)? [___] ___ ___

4.2.3 Did the absolute retention time of the internal standards $^{13}C_{12}$-1,2,3,4-TCDD exceed 25.0 minutes on the DB-5 column and 15.0 minutes on the DB-225 column? (Method 1613A, Section 7.2.4) [___] ___ ___

4.2.4 Are the relative retention times of native and labeled PCDD's and PCDF's within the limits given in Table 2 of the method. (Method 1613A, Section 14.4.1.2) [___] ___ ___

ACTION: If no for sections 4.2.2, 4.2.3 and 4.2.4, assess the effect on the validity of the data. Note in the Data Assessment.

4.2.5 For DB-5 or equivalent, (Method 1613A, Section 14.4.2.24) the peak separation between the unlabeled 2,3,7,8-TCDD and the peaks representing any other TCDD analyte shall be resolved with a valley of ≤ 25 percent.
Was this criteria met? [___] ___ ___

% Valley = (x/y) x (100)

Y = The peak height of 2,3,7,8-TCDD analyte

X = The distance from the baseline to the bottom of the valley between the adjacent peaks.

ACTION: If the percent valley criteria are not met, qualify all positive data "J". Do not qualify non-detects.

4.2.6 Is the last eluting tetra chlorinated congener (1,2,8,9-TCDD) and the first eluting penta chlorinated congener (1,3,4,6,8-PeCDF) separated properly, since they elute within 15 seconds of each other? [___] ___ ___

ACTION: If one of the congener is missing, report that in the Data Assessment.

5.0 Initial 5-Point Calibration

N/A

YES NO

The initial calibration standard solutions (CS1-CS5) must be analyzed prior to any sample analysis. However, initial calibration should be analyzed when the CS3 Calibration Verification (VER) or Isomer Specificity Test Standard do not meet performance criteria. The initial calibration standards must be analyzed on the same instrument using the same GC/MS conditions that were used to analyze the Window Defining Mixture and the Isomer Specificity Test Standards.

Was the initial calibration performed at the frequency specified above? [ ] ___

5.1 The method allows the Laboratory to perform quantitative analysis by isotope dilution and internal standard, or to combine calibration solutions.

1. Isotope Dilution: performed for the fifteen 2,3,7,8-substituted PCDDs and PCDFs unlabeled analytes with labeled analytes added to the samples prior to extraction and for 1,2,3,7,8,9- HXCDD and OCDF (see sections 5.2.8 and 5.2.9). The relative response (RR) is calculated and the percent coefficient of variation must be < 20% over the 5 point range to use the average response factor for quantitation, otherwise a calibration curve must be used..

2. Calibration by Internal Standard: performed for non-2,3,7,8 substituted compounds having no labeled analytes in this method and for measurement of labeled compounds for intra laboratory statistics.. The response factor (RF) is calculated and the percent coefficient of variation must be <35% over the 5 point range to use the average response factor for quantitation, otherwise a calibration curve must be used.

3. Combined Calibration: performed by using solutions containing unlabeled, labeled compounds and internal standards. The requirements of each of the above methods are used. This method allows the laboratory to produce a single set of curves for isotope dilution and internal standard method.

5.1.1 The following MS/DS conditions must be used:

5.1.1.1 Mass calibration as per Section 4.1? [ ] ___ ___

5.1.1.2 Were SIM data acquired for each of the ions listed in Table 3, including interfering ions? (see analytical method) [ ] ___ ___

5.2 Were the following GC criteria met?

5.2.1 The chromatographic resolution between the 2,3,7,8-TCDD and the peaks representing any other unlabeled TCDD isomers must be resolved with a valley of ≤ 25 percent on the primary analysis (DB-5) column (see sec. 14.4.2.2/ Pg. 29 of the method). [ ] ___ ___

5.2.2 The chromatographic resolution between the 2,3,7,8-TCDF and the peaks representing any other unlabeled TCDF isomers must be resolved with a valley of ≤ 25 percent on the confirmation (DB-225 or SP2330) analysis column. [ ] ___ ___

5.2.3 For all calibration solutions, the relative retention time of peaks representing an unlabeled 2,3,7,8- substituted PCDD or PCDF must be within the limits given in table 2 of the Method. The retention times of the peaks representing non-2,3,7,8- substituted PCDD or PCDF's must

N/A

YES NO

fall within the retention time windows established by the Window Defining Mixture. In addition, the absolute retention times of internal standards, $^{13}C_{12}$1,2,3,4-TCDD and $^{13}C_{12}$1,2,3,7,8,9-HxCDD shall not change by more than 15 seconds between the CS3 analysis and the analysis of any other standard. [ ] ___ ___

5.2.4 The two SIM ions for each homolog must maximize simultaneously and within 2 seconds of the corresponding labeled analyte ions. [ ] ___ ___

5.2.5 The relative ion abundance criteria for PCDDs/PCDFs listed in Table 3A (see analytical method) must be met. [ ] ___ ___

5.2.6 For all calibration solutions the signal to noise ratio (S/N) for the GC signal present in every SICP, including the ones for the labeled standards must be ≥ 10. [ ] ___

___

5.2.7 The percent relative standard deviations (% RSD) for the mean response factors (RRF) from the 17 unlabeled standards must be ≤ 20%, and those for the 15 labeled reference compounds must be ≤ 35%. [ ] ___ ___

5.2.8 Labeled analyte 1,2,3,7,8,9-HxCDD is used as an internal standard in this method, and can not be used to quantitate corresponding unlabeled analyte. The unlabeled 1,2,3,7,8,9-HxCDD must be quantitated using the average of the responses of the labeled analytes of 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD. The concentration of the unlabeled 1,2,3,7,8,9-HxCDD is corrected for the average recovery of the other HxCDD's. Was the unlabeled 1,2,3,7,8,9-HxCDD quantitated correctly? [ ] ___ ___

5.2.9 The labeled analog of OCDF is not added to the sample because of a potential interference. Unlabeled OCDF is quantitated against the labeled OCDD. The concentration of the unlabeled OCDF is corrected for the recovery of the labeled OCDD. Was the unlabeled OCDF correctly quantitated against the labeled OCDD. [ ] ___ ___

ACTION:

1. If mass calibration criteria as specified in Section 4.1 was not met, note in Data Assessment.

2. If the selected monitoring ions specified in Table 3 were not used for data acquisition, the lab must be contacted by the Project Officer for an explanation. If an incorrect ion was used, reject "R" all the associated data.

3. If the 25% percent valley for TCDD requirement was not met, quality positive data "J". Do not qualify non-detects. The tetra and penta (dioxins and furans) are affected. Heptas, Hexas and Octas are not affected.

4. If the ion abundance ratio for an analyte is outside the limits, flag the results for that analyte "R" (reject).

5. If the ion abundance ratio for an internal or labeled standard falls outside the QC limits flag the associated positive hits with "J". No effect on the non-detects.

YES NO

N/A

6. If the signal to noise ratio (S/N) is below control limits, use professional judgement to determine quality of the data.

7. If the %RSD for each unlabeled analyte exceeds 20%, or the %RSD for each labeled analyte exceeds 35%, flag the associated sample positive results for that specific analyte as estimated ("J"). No effect on the non-detect data.

8. If 1,2,3,7,8,9-HxCDD was not calculated using the correct HxCDD response (average) factor, either manually recalculate the values for all standards and samples or contact Project Officer to request resubmittals from the laboratory.

9. If OCDF was not calculated using the correct response factor (OCDD), either manually recalculate the values for all standards and data or contact Project Officer to request resubmittals from the laboratory.

10. Non compliance of any other criteria specified above should be evaluated using professional judgement.

5.2.10 Spot check response factor calculations and ion ratios. Ensure that the correct quantitation ions for the unlabeled PCDDs/PCDFs and labeled standards were used. In addition, verify that the appropriate labeled standard was used for each analyte.

To recalculate the response factor, use the equation:

For target compounds (unlabeled analytes with corresponding labeled analytes):

$$RR = \frac{(A_{n1} + A_{n2}) \times Q_l}{(A_{l1} + A_{l2}) \times Q_n}$$

For labeled analytes, Internal standards and cleanup standard listed in Table 6 of method 1613:

$$RF = \frac{(A_{l1} + A_{l2}) \times Q_{is}}{(A_{is1} + A_{is2}) \times Q_l}$$

Note. There is only one m/z for $^{37}Cl_4$2,3,7,8-TCDD.

$A_{n1} + A_{n2}$ = integrated areas of the two quantitation ions of analytes of interest. (Target analyte, unlabeled compounds)

$A_{l1} + A_{l2}$ = integrated areas of the two quantitation ions of the appropriate labeled analytes compound.

$A_{is1} + A_{is2}$= integrated areas of the two quantitation ions of the appropriate internal standard.

Q_n = quantity of the unlabeled PCDD/PCDF analyte injected [pg]

Q_l = quantity of the appropriate labeled analytes compound [pg]

Q_{is} = quantity of the appropriate internal standard injected [pg]

ACTION: 1. If calculations were not performed correctly, notify the Project Officer to initiate

N/A

YES NO

resubmittals from the laboratory.

6.0 System and Laboratory Performance (Calibration Verification and Isomer Specificity Test Standard)

At the beginning of a 12 hour shift during which analyses are performed, GC/MS system performance and calibration are verified for all unlabeled and labeled compounds. For these tests the calibration verification (VER) standard and the isomer specificity test standards shall be used to verify all performance criteria.

Only if the laboratory meets all performance criteria may samples, blanks, and precision and recovery standards be analyzed.

6.1 Calibration Verification

6.1.1 Was the relative ion abundance for PCDDs/PCDFs listed in Table 3A of the analytical method met? (Method 1613A, Section 14.3.2) [___] ___ ___

6.1.2 Were the peaks representing each unlabeled and labeled compound in the verification standard present with signal to noise ratio (S/N) of $\geq$ 10? (Method 1613A, Section 14.3.3) [___] ___ ___

6.1.3 For each compound, was the concentration within the limit in Table 7 of the method? (Method 1613A, Section 14.3.5) [___] ___ ___

6.1.4 Were the absolute retention time of the internal standards $^{13}C_{12}$-1,2,3,4- TCDD and $^{13}C_{12}$1,2,3,7,8,9- HxCDD within $\pm$ 15 seconds of the retention times obtained during calibration? (Method 1613A, Section 14.4.1.1) [___] ___ ___

6.1.5 Were the relative retention times of the unlabeled and labeled PCDDs and PCDFs within the limits given by Table 2 of the method? (Method 1613A, Section 14.4.2.2) [___] ___ ___

6.2 Isomer Specificity Test Standard

6.2.1 Was the chromatographic resolution between 2,3,7,8-TCDD and the peaks representing any other unlabeled TCDD isomers resolved with a valley of $\leq$ 25 percent on the primary analysis (DB-5) column? (Method 1613A, Section 14.4.2.2) [___] ___ ___

6.2 Was the chromatographic resolution between 2,3,7,8- TCDF and the peaks representing any other unlabeled TCDF isomers resolved with a valley of $\leq$ 25 percent on the confirmation (DB-225 or SP2330) analysis [___] ___ ___

ACTION:

1. If the ion abundance ratio for an analyte is outside the limits, flag the results for that analyte "R" (reject).

2. If the signal noise ratio (S/N) is below control limits, use professional judgement to determine the quality of the data.

N/A

YES NO

3. If an analyte concentration fell outside the acceptance criteria listed in Table 7 of the method.

   A. If the acceptance criteria for each unlabeled analyte and/or for each labeled analyte exceeds the range, flag the associated sample positive results for that specific analyte as estimated ("J"). No effect on the non-detect data.

   B. If the acceptance criteria for each unlabeled analyte and/or for each labeled analyte is below the range, flag the associated sample positive results as well as non-detects for that specific analyte as estimated ("J").

   C. If the acceptance criteria for each unlabeled analyte and/or for each labeled analyte is excessively below, $\leq$ 10% of the range, at the minimum, flag the associated sample positive results as well as non-detects for that specific analyte as estimated ("J"). However the validator may use professional judgement to accept or reject positive data and non-detects.

4. If the 25 percent valley for TCDD and TCDF requirement was not met, qualify positive data "J". Do not qualify non-detects. The tetras and pentas (dioxin and furans) are affected. Heptas, Hexas and Octas are not affected.

5. Non compliance of any other criteria specified above, in the method should be evaluated using professional judgement.

6.3 Spot check response factor calculations and ion ratios. Ensure that the correct quantitation ions for the unlabeled PCDDs/PCDFs and labeled standards were used. In addition, verify the appropriate labeled standard was used for each analyte.

7.0 Sample Data

NOTE: Any qualifications such as "J" applied to target compounds should be also applied to their associated total congeners concentration column.

7.1 Were the following MS/DS conditions used?

7.1.1 SIM data were acquired for each of the ions listed in Table 3 (see analytical method) including diphenylether interfering ions. [ ] ___ ___

7.2 Were the following identification criteria met?

7.2.1 For the 2,3,7,8 substituted analytes found present and the corresponding labeled compound or internal standard in the sample extract, must show relative retention times at the peak height within the limits given in Table 2. (Method 1613A, Section 15.4) [ ] ___ ___

7.2.2 For non-2,3,7,8 substituted compounds (tetra through octa) found present, the retention time must be within the window established by the Window Defining Mixture, for the corresponding homologue. (Method 1613A, Section 15.4) [ ] ___ ___

7.2.3 All specified ions listed in Table 3 for each isomer found present and the associated labeled compounds must be present in the SICP. The two SIM ions for the analyte, the labeled compound, and the internal standard must maximize simultaneously.(+ 2 sec.)

N/A		YES	NO
	(Method 1613A, Section 15.1)	[ ]	
7.2.4	The integrated ion current for each characteristic ion of the analyte identified as positive, must be at least 2.5 times background noise and must not have saturated the detector. (Method 1613A, Section 15.2)	[ ]	
7.2.5	The integrated ion current for the labeled compounds, internal standards, and cleanup standard characteristic ions must be at least 10 times background noise. (Method 1613A, Section 15.2)	[ ]	
7.2.6	The relative ion abundance criteria for all PCDDs/PCDFs found present must be met. (Table 3A - Method 1613A, Section 15.3)	[ ]	
7.2.7	The relative retention time of the unlabeled 2,3,7,8-substituted PCDD or PCDF must be within the limits given in Table 2 (Method 1613A).	[ ]	
7.2.8	The relative ion abundance criteria for the labeled compounds, cleanup, and internal standard must be met (Table 3A - Method 1613A).	[ ]	
7.2.9	The analyte concentration must be within the calibration range. If not, dilution should have been made to bring the concentration within the calibration range. Was this criterion met?	[ ]	
NOTE:	The analytical method clearly states that samples containing analytes having concentrations higher than 10 times the upper MCLs should be analyzed using a less sensitive, high resolution GC/low resolution MS method.		
7.2.10	The identification of a GC peak as a PCDF can only be made if no signal having a S/N ≥ 2.5 is detected at the same time in the corresponding polychlorinated diphenylether (PCDPE) channel. Was the above condition met?	[ ]	

ACTION:

1. If the selected monitoring ions specified in Table 3 were not used for data acquisition, the lab must be contacted by the Project Officer for an explanation. If an incorrect ion was used, reject "R" all the associated data.

2. If the retention time of an analyte falls outside the retention time windows established by the associated Window Defining Mixture take the following action:

   A. If the analyte has a corresponding labeled analyte and is within 2 seconds of the labeled analyte, no action taken on positive data or non-detects.

   B. If the analyte has a corresponding labeled analyte and is outside 2 seconds of the labeled analyte, use professional judgement to determine qualifications for positive data or non-detects. At a minimum, "J" or "JN" positive data.

   C. If the analyte does not have a corresponding labeled analyte and is outside 2 seconds of the matching unlabeled analyte from the associated calibration, use professional judgement to determine qualifications for positive data or non-detects. At a minimum, "J" or "JN" positive data.

YES NO

N/A

D. If analyte meets identification criteria (7.2.2, 7.2.4, 7.2.5, 7.2.7) but does not meet ion abundance ratio criteria (7.2.8) and is not a labeled analog, the sample must be reanalyzed on a confirmation column. If confirmation analysis was not perform, reject the failing analyte.

3. If the criteria listed in section 7.2.4 and 7.2.5 are not met but all other criteria are met, qualify all positive data of the specific analyte with "J".

4. If the analytes reported positive do not meet criteria for section 7.2.6, reject (R) all positive data for these analytes. Change the positive values to EMPC (Estimated Maximum Possible Concentration). Flag "J"

5. If the labeled compounds, internal standards and cleanup standards do not meet ion abundance criteria section 7.2.6. and 7.2.7. (Table 3 - analytical method) but they meet all other criteria, flag all corresponding data with "J".

6. If the lab reported values exceeding the calibration range flag those values with "J".

7. If peak deflections >50% are visible qualify particular compound with "J".

8. If PCDF was detected but an interfering PCDPE was also detected (see Section 7.2.9) and concentration not corrected for the interference, cross out the PCDF data. The reported value of PCDF is changed to EMPC.

9. If the lab did not monitor for PCDPEs, qualify all positive furan data "JN".

7.2.10 Spot check calculations for positive data and verify that the same labeled compounds used to calculate RFs were used to calculate concentration and EMPC. Ensure that the proper PCDDs/PCDFs and labeled compounds were used.

To recalculate the concentration of individual PCDD/PCDF analytes in the sample use the following equation:

All Matrices other than water

$$Cn\ (pg/g) = \frac{(A_{n1} + A_{n2}) \times Q_l}{W \times (A_{l1} + A_{l2}) \times RR}$$

Water

$$Cn\ (pg/L) = \frac{(A_{n1} + A_{n2}) \times Q_l}{V \times (A_{l1} + A_{l2}) \times RR}$$

Where:

$A_{n1} + A_{n2}$ = integrated areas of the two quantitation ions of analyte of interest. (Target analyte)

$A_{l1} + A_{l2}$ = integrated areas of the two quantitation ions of the appropriate labeled analyte compound.

W = Weight (g) of sample extracted

V = Volume (L) of sample extracted

YES NO

N/A

Q_i = Quantity (pg) of the appropriate labeled compound added to the sample prior to extraction.

RR = Calculated relative response from initial calibration. (see section 5.2.10)

ACTION: If the spot check calculations yielded positive hit concentrations with ≤ 15% Difference from those reported in Form I, correct manually. If the difference between the validator's value and the form 1's values are > 15% contact the Project Officer to request from the laboratory for an explanation and a copy of the laboratory's calculations.

7.3 Clean-up procedures

Clean-up may not be necessary for relatively clean samples (drinking waters, ground waters etc). If the matrix required clean-up, the laboratory has 4 different procedures to choose from. Before using any clean-up procedure, the laboratory must demonstrate that the Initial Precision and Recovery requirements of the method can be met using the clean-up procedure.

A labeled clean-up standard $^{37}Cl_4$2,3,7,8-TCDD is added to the sample just before the back extraction with base and acid procedure. This occurs before any recommended clean-up procedures are initiated.

7.3.1 Was the percent recovery of the clean-up standard within the recommended range of 25-150% for each sample? [ ] ___ ___

ACTION: If no, and the recovery is less than 25%, qualify all data as estimated "J". If recovery is 0 %, qualify all positive data as estimated "J" and reject "R" all non-detects for that sample.

7.3.2 Check the chromatograms that clean-up procedure was needed for each sample. Were any clean-up procedures needed for either water or soil samples? ___ [ ] ___

ACTION: If yes, check extraction log to verify which clean-up procedures if any were performed. The laboratory is not limited to only one procedure.

1. If no clean-up was performed and the chromatograms indicated that some should have been performed. Use professional judgement to assess the effect on the interference on the validity of the data. Document lack of required clean-up for complex samples in Data Assessment.

2. If one type of clean-up was performed, but the chromatograms indicate that additional clean-up should have been utilized. Use professional judgement to assess the effect on the interference on the validity of the data. Document lack of additional clean-up for complex samples in Data Assessment.

7.3.3 If clean-up procedures were used, did the Laboratory perform clean-up procedures on the Initial Precision and Recovery samples as required by the method? [ ] ___ ___

ACTION: If no, Use professional judgement to assess the effect of the interference on the validity of the data. Document lack of IPR documentation for clean-up procedures in Data Assessment.

8.0 Estimated Detection Limits (EDL) ***If required for the project***

8.1 Was an EDL calculated for each 2,3,7,8-substituted analyte that was not identified regardless

N/A

YES NO

of whether other non-2,3,7,8 substituted analytes were present? [___] ___ ___

ACTION: 1. If EDL or EMPC of an analyte which was not reported as a positive hit is missing, correct manually or contact the Project Officer to request from the laboratory corrections.

8.2 Use the equation below to check EDL calculations:

ALL MATRICES OTHER THAN WATER

$$EDL\ (pg/g) = \frac{2.5 \times Qis \times (Hx^1 + Hx^2) \times D}{W \times (His^1 + His^2) \times RR}$$

WATER

$$EDL\ (pg/L) = \frac{2.5 \times Qis \times (Hx^1 + Hx^2) \times D}{V \times (His^1 + His^2) \times RR}$$

Where:

Hx^1 and Hx^2 = peak heights of the noise for both quantitation ions of the 2,3,7,8-substituted isomer of interest.

His^1 and His^2 = peak heights of both the quantitation ions of the appropriate internal standards.

D = dilution factor

Qis, RR, W and V are previously defined.

NOTE: The validator should check the EDL data to verify that peak heights and not areas were used for this calculation. If the area algorithm was used, the validator should contact the Project Officer to request recalculations from the laboratory.

ACTION: If the spot check calculations yielded EDLs or EMPCs with $\leq$ 15% Difference from those reported in Form I, correct manually. If the difference between the validator's value and the Form I's values are > 15% contact the Project Officer to request from the laboratory for an explanation and a copy of the laboratory's calculations.

9.0 Estimated Maximum Possible Concentration (EMPC) *If required for the project*

9.1 Was an EMPC calculated for 2,3,7,8-substituted analytes that had S/N ratio for the quantitation and confirmation ions greater than 2.5, but did not meet all the identification criteria? [___] ___ ___

9.2 Use the equation below to check EMPC calculations:

All Matrices other than water

$$EMPC\ (pg/g) = \frac{(A_{n1} + A_{n2}) \times Q_i \times D}$$

YES NO

N/A

Water:

$$W \times (A_{l1} + A_{l2}) \times RR$$

$$EMPC\ (pg/L) = \frac{(A_{n1} + A_{n2}) \times Q_i \times D}{V \times (A_{l1} + A_{l2}) \times RR}$$

Action: 1. If EDL or EMPC of an analyte which was not reported as a positive hit is missing, correct manually or contact the Project Officer to request from the laboratory corrections.

2. If the spot check calculations yielded EDLs or EMPCs with ≤ 15% Difference from those reported in Form I, correct manually. If the difference between the validator's value and the Form I's values are > 15% contact the Project Officer to request from the laboratory for an explanation and a copy of the laboratory's calculations.

3. If EDLs or EMPCs for the most toxic analytes (TEF ≥ 0.05) are above reporting limits, contact the project office to recommend sample reanalysis.

10.0 Method Blanks

10.1 Has a method blank per matrix been extracted and analyzed with each batch of 20 samples? [___] ___ ___

10.2 If samples of some matrix were analyzed in different events (i.e. different shifts or days) has one blank for each matrix been extracted and analyzed for each event? [___] ___ ___

10.3 Acceptable method blanks must not contain any signal of 2,3,7,8-TCDD, or 2,3,7,8-TCDF, equivalent to a minimum levels listed in Table 2 (> 1 ng/Kg for soils, and 10 pg/L for water). Was this criteria met? (Method 1613A, Section 8.5.2) [___] ___ ___

10.4 For other 2,3,7,8- substituted PCDD/PCDF isomers of each homologue, the allowable concentration in the method blank is less than minimum level listed in Table 2 (< 5 ng/Kg for soils and 50 pg/L for waters). Was this criteria met? [___] ___ ___

ACTION: 1. If the proper number of method blanks were not analyzed, document in Data Assessment. If the validator feels that the validity of the data is seriously compromised and validation of data without the method blanks would be flawed then notify the Project Officer. If decision is made to proceed with the validation process, consider the following actions: no action taken on non-detected analytes. If an analyte has a reported concentration that is > 5 times the EDL, qualify "J" and all concentrations ≤ 5 times the EDL are qualified "R" due to possibility of contamination.

2. If the method blank is contaminated with 2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD, 1,2,3,7,8-PeCDF or 2,3,4,7,8-PeCDF at a concentration higher than the minimum levels in Table 2, reject all contaminant compound positive data for the associated samples "R" and notify the Project Officer to initiate reanalysis.

3. A. If the method blank is contaminated with any of the analytes mentioned in Action # 2 at a concentration of less than the minimum levels in Table 2 specified in the method or of any other 2,3,7,8-substituted analytes at any concentration and the concentration in the sample is less than five times the concentration in the blank,

YES NO

N/A

transfer the sample results to the EMPC/EDL column and cross-out the value in the concentration column in order to present the data as a non-detect.

B. If the concentration in the sample is higher than five times the contamination concentration in the blank, no action is needed.

11.0 Labeled Compound Recoveries

11.1 Were the samples spiked with all the labeled compounds as specified in the method? [___] ___ ___

11.2 Have labeled compounds' recoveries been within the required (25 - 150%) limits? [___] ___ ___

11.3 If not, were samples reanalyzed? [___] ___ ___

ACTION: 1. If the labeled compound recovery was below 25 percent, reject "R" all associated non- detect data (EMPC/EDL) and flag with "J" the positive data for the associated compound.

2. If the labeled compound recovery is above the upper limit (150 percent) flag associated positive data with "J". No effect on non-detects.

3. If the labeled compound recovery is less than 10%, qualify positive hits and non-detects associated with the failed labeled compound "R" (Reject). When highly toxic analytes (TEF$\geq$ 0.05) are affected, notify Project Officer to initiate reanalysis.

Recalculate the percent recovery for each labeled standard in the sample extract, Rec_l, using the formula:

$$\%\ Rec_l = \frac{(A_{l1} + A_{l2}) \times Q_{is} \times 100}{(A_{is1} + A_{is2}) \times RF \times Q_l}$$

$A_{l1} + A_{l2}$ = integrated areas of the two quantitation ions of the appropriate labeled compound.

$A_{is1} + A_{is2}$ = integrated areas of the two quantitation ions of the appropriate internal standard.

Q_l = quantity of the appropriate labeled compound

Q_{is} = quantity of the appropriate internal standard injected

RF was defined, previously.

12.0 Internal Standard Area Response

There is no method criterion for the Internal Standard area response. However, because it is very critical in determining instrument sensitivity, the Internal Standard area response should be checked for every sample. The two standards $^{13}C_{12}$1,2,3,4-TCDD and $^{13}C_{12}$1,2,3,7,8,9-HxCDD are referred to as Internal Standards in this method. In other Dioxin methods, the two standards are called Recovery Standards.

12.1 Are the internal standard areas for every sample and blank within the upper and lower limits of each associated initial calibration CS3?

N/A

YES NO

Area upper limit= +100% of internal standard area.
Area lower limit= -50% of internal standard area. [ ] ___ ___

12.2 Is the retention time of each internal standard within 15 seconds of the associated initial calibration CS3 standard? [ ] ___ ___

ACTION: 1. If the internal standard area is outside the upper or lower limits, flag all related positive and non-detect data (EMPC/EDL) with "J" regardless whether the lab's labeled compound recoveries met specifications or not.

2. If extremely low area counts (<25%) are reported, flag all associated non-detect data as unusable "R" and the positive data "J".

3. If the retention time of the internal standards differs by more than 15 seconds from the initial calibration CS3, use professional judgement to determine the effect on the results. A time shift of more than 15 seconds may cause certain analytes to elute outside the retention time window established by the GC window defining/column performance check solution. A constant shift could be also the result of a leak.

NOTE: Action 1 and 2 are recommendations only since this criterion is not a method requirement. These guidelines are based on other methods, previously validated data packages and Region II recommendations. If method blanks have low area responses as well as the samples, the validator should seriously consider qualifying the data for this criterion. Action 3 is a method requirement.

13.0 Second Column Confirmation

13.1 Any sample in which 2,3,7,8-TCDF is identified on a DB-5 column, must have a confirmation analysis (Method 1613A, section 15.2). Was a second column confirmation performed? [ ] ___ ___

13.2 Was the sample extract reanalyzed on a 30 m DB-225, fused silica capillary column, for 2,3,7,8-TCDF using the GC/MS conditions given in Section 7.9.7.1.2 of the analytical method? [ ] ___ ___

NOTE: The concentration of 2,3,7,8-TCDF obtained from the primary column (DB-5) should only be used for qualification, due to better QC data associated with the primary column. Also note that the confirmation and quantitation of 2,3,7,8-TCDF may be accomplished on a SP-2330 GC column.

ACTION: If confirmation is missing, use professional judgement, or contact the Project Officer for assistance.

13.3 Did the second column meet the calibration and linearity specification in Sections 5.0 and 6.0 above? [ ] ___ ___

ACTION: If no, refer to section 5.0 and 6.0 for appropriate action.

13.4 Was the % D of the quantitation results of the two columns less than 50? [ ] ___ ___

ACTION: Note in data assessment the differences, use professional judgement to decide which column data to report for TCDF. No other action is needed since this is not a method requirement

YES NO

N/A

but a technical recommendation.

14.0 Sample Reanalysis

14.1 The Project Officer will evaluate the need for reanalyzing the samples with qualified data based on site-specific Data Quality Objectives.

14.2 Due to a variety of situations (see below) that may occur during sample analysis, the laboratory is required to reanalyze or re-extract and reanalyze certain samples. If a reanalysis was required but was not performed, contact the Project Officer to initiate reanalysis. List in data assessment all re-extractions and reanalyses and identify the PCDD/PCDF sample data summaries which must be used by the data user (when more than one analysis is submitted for a sample).

Lab must re-extract and/or re-analyzed samples when the following criteria are not met:

1. Contaminated method blank at concentrations above the minimum levels (Table 2)
2. Labeled compound recoveries outside acceptable range of 25-150%.
3. Exceedance of calibration range by an analyte (dilution or re-extract using a smaller aliquot).
4. Recovery of labeled compounds outside acceptable limits (25-150%) in a diluted sample (re-extracted using a smaller aliquot).

ACTION: For criteria 1, 2, or 3, notify the Project Officer to discuss possible re-analysis of sample by the laboratory.

For criteria 4, If the calibration was verified and the re-extracted sample still does not meet labeled recovery requirements (25-150%), then the method does not apply to the sample. The results are not reportable for regulatory purposes (Method 1613A, section 17.2). Notify the Project Officer of problem to initiate re-analysis of sample using a different method. Document in Data Assessment.

15.0 Precision and Recovery (PAR)

The laboratory is required to show initial demonstration of capability, to evaluate and document data quality. Laboratory performance is compared to established performance criteria to determine if results of analyses meet the performance characteristics of the method.

The laboratory must perform and submit data to establish the ability to generate acceptable precision and accuracy.

15.1 Did the laboratory analyzed an Initial Precision and Recovery (IPR) standard as outlined in section 8.2 required by the method? [___] ___ ___

ACTION: If no, contact the Project Officer to request resubmittals from the laboratory.

If data is not available, discuss with the Project Officer the feasibility of continuing with validation. If a decision is made to proceed with validation, use professional judgement. All data at a minimum should be qualified as estimated "J". Technically according to the method, data and system performance is unacceptable for all compounds. Analyses should not have continued as per the

N/A YES NO

method. Document under contract non-compliance in Data Assessment.

15.2 Did the IPR standard deviation (s) and average concentration (x) passed criteria as outlined in Table 7 of the method? [___] ___ ___

ACTION: If no, refer to action from section 15.1.

NOTE: The concentration limits in Table 7 for labeled compounds are based on the requirements that the recovery of each labeled compound be in the range of 25-150%.

The laboratory must analyzed an Ongoing Precision and Recovery standard (OPR) periodically, at the beginning of 12 hour shift after the analysis of the CS3 calibration verification (VER), and before the analysis of any sample in each set .

15.3 Was the Ongoing Precision and Recovery (OPR) standard analyzed at the required frequency? [___] ___ ___

15.4 Did the OPR standard passed the concentration criteria limits in Table 7 of the method? [___] ___ ___

ACTION: If no, refer to action from section 15.1. All samples that do not have a passing OPR standard are potentially affected for that analyte.

The following sections may be incorporated in the validation process on a case by case basis depending upon the requirements of the Project Plan. Sometimes a laboratory will provide data for some of the following sections on a routine basis. If not a requirement of the Project Plan, then professional judgement is needed to qualify data based on additional information.

16.0 Isomer Specificity and Toxicity Equivalency Factor (TEF)

NOTE: The TEF value concentrations can be found in the DFLM01.1 Statement of Work for Dioxin Analysis Form I PCDD-2.

When calculating the 2,3,7,8-TCDD Toxicity Equivalency of a sample only those 2,3,7,8 substituted isomers that were positively identified in the sample must be included in the calculations. The sum of the TEF adjusted concentration is used to determine when a second column confirmation is required to achieve analyte specificity.

16.1 Did the lab include EMPC or EDL values in the toxicity equivalency calculations? [___] ___ ___

16.2 Were all samples, whose toxicity equivalency exceeded the required values were reanalyzed on a confirmation column to establish analyte specificity? [___] ___ ___

ACTION: 1. If yes, the toxicity equivalency calculations were not calculated properly, notify the Project Officer to arrange for laboratory resubmittals.

2 If the toxicity equivalency exceeded the required limits (0.7 μg/Kg for soil/ sediment, 7 ng/L for aqueous and 7 μg/Kg for chemical waste samples), and the lab failed to reanalyze the samples on a specific secondary column, notify Project Officer. Reanalysis may be initiated.

NOTE: Any qualifications such as "J" applied to target compounds should be also applied to their associated total congeners concentration.

17.0 Rinsate Blank *(Region 2 QA guidelines recommend rinse blanks for all projects)*

N/A

YES NO

17.1 One rinsate blank should be collected for each batch of 20 soil samples or one per day whichever is more frequent. Were rinsate blanks collected at the above frequency? [ ] ___ ___

17.2 Do any rinsate blanks show the presence of 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 1,2,3,7,8-PeCDD at amounts > .5 μg/L or any other analyte at levels > 1 μg/L? [ ] ___ ___

ACTION: If any rinsate blank was found to be contaminated with any of the PCDDs/PCDFs notify the Project Officer to discuss what proper action must be taken.

If any qualification is needed due to rinsate blank contamination, follow the guidelines outlined under Method Blanks, section 10, Actions 2 and 3.

18.0 Field Blanks

18.1 The field blanks are PEM samples (blind blanks) supplied to Laboratory at the frequency of one field blank per 20 samples or one per samples collected over a period of one week, which ever comes first. A typical "field blank" will consist of uncontaminated soil. The field blanks are used to monitor possible cross contamination of samples in the field and in the laboratory.

Were the following conditions met?

18.2 Acceptable field blanks must not contain any signal of 2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD and 1,2,3,7,8-PeCDF equivalent to a concentration of > 20 ng/Kg. [ ] ___ ___

18.3 For other 2,3,7,8 substituted PCDD/PCDF analytes of each homologue the allowable concentration in the field blank is less than the upper MCLs listed in the method. [ ] ___ ___

ACTION: When the field blank is found to be contaminated with target compounds, apply the same action as described for the Method Blank, section 10, Actions 2 and 3.

NOTE: Ask Project Officer to verify that the PEM blank (field blank) did not contain any PCDD/PCDF analytes and ask their assistance in the evaluation of the PEM field blank.

19.0 PEM Interference Fortified Blanks

NOTE: This type of blank may not be available at this time. In many cases, laboratories will substitute matrix spike/matrix spike duplicate (MS/MSD). If a PEM Interference Fortified blank(s) were not analyzed but MS/MSD data were submitted, skip this section and go onto to section 21.

19.1 One known blank usually an interference fortified soil/sediment sample is supplied to the Laboratory. The frequency of this QC sample is one per group of 20 environmental samples or one per samples collected over one week period, whichever occurs first. The sample is spiked by the laboratory with the appropriate volume of the matrix spiking solution and then extracted and analyzed with other samples.

19.2 Was a fortified PEM blank analyzed at the frequency described above? [ ] ___

___

N/A

YES NO

19.3 Was the percent recovery of 2,3,7,8-TCDD and other 2,3,7,8-substituted compounds within the 50 to 150 percent control limits? [ ] ___ ___

ACTION: 1. If the recovery of a 2,3,7,8-substituted analytes falls outside the 50-150 percent control limit, flag all positive and non-detect data of the same and related analytes in the same homolog series with "J". However, if the recovery is below 20%, qualify all associated non-detects "R" and positive hits as "J". Notify the Project Officer. Reanalysis may be initiated.

2. If no fortified PEM blank was analyzed, use professional judgement to assess data validity.

20.0 Matrix Spike (MS) Field Sample

Note: Matrix spike is not required by this method although Labs may routinely perform this analysis as part of internal QA/QC and submit this data as part of the package. Verify requirements with Project Officer.

20.1 Was a matrix spike analyzed at the frequency of one per SDG samples per matrix? [ ] ___ ___

20.2 Was the percent recovery of 2,3,7,8-TCDD and other 2,3,7,8-substituted PCDDs/PCDFs within 60 to 140 percent? [ ] ___ ___

ACTION: If problems such as interferences are observed, use professional judgement to assess the quality of the data. The 60-140% limits of the matrix spike data may be used to flag data of the spiked sample only. The matrix spike data of the PE blank sample are more important and must be used primarily in data validation.

20.3 Was a matrix spike duplicate analyzed as per section 11.1 and 11.2? [ ] ___ ___

ACTION: No action required. A matrix spike duplicate is not required. Use professional judgement if there is a large difference in concentrations reported between MS and MSD. Qualifications if any, can only be performed on the sample that was used for this criteria.

21.0 Environmental Duplicate Samples *(recommended in Region 2 for all Projects)*

NOTE: Do not confuse an environmental duplicate with a matrix spike duplicate. An environmental duplicate is a sample that has been divided into 2 parts (extracted and analyzed as two different samples) or as 2 separate samples from the same location sent by the sampling crew. This sample is not spike with any additional compounds other than those compounds required by the method for analysis of all routine samples.

21.1 For every batch of 20 samples or samples collected over a period of one week, whichever is less, there must be a sample designated as duplicate. Were duplicate samples collected at the above frequency? [ ] ___ ___

21.2 Did results of the duplicate samples agree within 25% relative difference for 2,3,7,8-substituted analytes and 50% for the rest of the analytes? [ ] ___ ___

ACTION: The duplicate results can be used in conjunction of other QC data. Use professional judgement.

N/A **YES NO**

22.0 REFERENCES

The following references are cited in Method 1613. They are important references for technical information and are submitted here as part of this method's documentation.

1. "Analytical Procedures and Quality Assurance Plan for the Determination of PCDD/PCDF in Fish", USEPA Environmental Research Laboratory, 6201 Congdon Boulevard, Duluth, NH 55804, April 1988.

2. Barnes, Donald G., Kutz, Frederick W., and Bottimore, David P., "Update of Toxicity Equivalency Factors (TEFs) for Estimating Risks Associated with Exposure to Mixtures of Chlorinated Dibenzo-p-dioxins and dibenzofurans (CDDs/CDFs)", Risk Assessment Forum, USEPA, Washington, DC 20460, February 1989.

3. Lamparski, L.L., and Nestrick, T.J., "Determination of Tetra-, Hexa-, Hepta-, and Octachlorodibenzo-p-dioxin Isomers in Particulate Samples at Parts per Trillion Levels", Analytical Chemistry, 52: 2045-2054, 1980.

4. "Measurment of 2,3,7,8-Tetrachlorinated Dibenzo-p-dioixin (TCDD) and 2,3,7,8-Tetrachlorinated Dibenzofurans (TCDF) in Pulp, Sludges, Process Samples and Waste-waters from Pulp and Paper Mills", Wright State University, Dayton, OH 45435, June 1988.

5. Method 1613-Revision A- Tetra through Octa- chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, USEPA, Washington, DC, 20460, October 1990

6. "Method 613--2,3,7,8-tetrachlorodibenzo-p-dioxin", 40 CFR 136 (49 FR 43234), October 26, 1984, Section 4.1.

7. "NCASI Procedures for the Preparation and Isomer Specific Analysis of Pulp and Paper Industry Samples for 2,3,7,8 TCDD and 2,3,7,8 TCDF", National Council of the Paper Industry for Air and Stream Improvement, 260 Madison Avenue, New York, NY 10016, Technical Bulletin No.551, Pre-release Copy, July 1988.

8. Provost, L.P., and Elder, R.S., "Interpretation of Percent Recovery Data", American Laboratory, 15: 56-83, 1983

9. Stanley, John S., and Sack, Thomas M., "Protocol for the Analysis of 2,3,7,8-Tetrachlorodibenzo-p-dioxin by High Resolution Gas Chromatography/High Resolution Mass Spectrometry", USEPA EMSL, Las Vegas, Nevada 89114, EPA 600/4-86-004, January 1986.

10. Tondeur, Yves, "Method 8290: Analytical Procedures and Quality Assurance for Multimedia Analysis of Polychlorinated Dibenzo-p-dioixin and Dibenzofurans hy High Resolution Gas Chromatography/High Resolution Mass Spectrometry", USEPA ENSL, Las Vegas, Nevada, June 1987.

11. Tondeur, Yves, "Proposed GC/MS Methodology for the Analysis of PCDDs and PCDFs in Special Analytical Services Samples", Triangle Laboratories, Inc., 801-10 Capitola Dr., Research Triangle Park, NC 27713, January 1988; updated by personal communication September 1988.

ATTACHMENT A

PCDFs/PCDD DATA ASSESSMENT

SDG No.
LABORATORY:
SITE:

DATA ASSESSMENT

The current Functional Guidelines for evaluating dioxin/furans organic data have been applied.

All data are valid and acceptable except those analytes which have been qualified with a "J" (estimated), "N" (presumptive evidence for the presence of the material), "U"(non-detects), "R" (unusable), or "JN"(presumptive evidence for the presence of the material at an estimated value). All action is detailed on the attached sheets.

Two facts should be noted by all data users. First, the "R" flag means that the associated value is unusable. In other words, due to significant QC problems, the analysis is invalid and provides no information as to whether the compound is present or not. "R" values should not appear on data tables because they can not be relied upon, even as a last resort. The second fact to keep in mind is that no compound concentration, even if it has passed all QC tests, is guaranteed to be accurate. Strict QC serves to increase confidence in data but any value potentially contains error.

Reviewer's
Signature:_____ Date:__/__/199_

Verified By:_____ Date:__/__/199_

GENERAL COMMENTS:

HOLDING TIME:

BLANK CONTAMINATION:

WINDOW DEFINING MIXTURE:

ION ABUNDANCE:

CALIBRATIONS:

RESOLUTION:

LABELED STANDARDS PERFORMANCE:

INTERNAL STANDARDS:

PEAK IDENTIFICATION:

MATRIX SPIKE/ ENVIRONMENTAL DUPLICATE:

CONFIRMATIONS:

OTHER QC OUT OF SPECIFICATION:

SYSTEM PERFORMANCE AND OVERALL ASSESSMENT:

CONTRACT PROBLEMS NON-COMPLIANCE:

RE-EXTRACTION, REANALYSIS OR DILUTIONS:

DO NOT USE **USE**

FIELD DOCUMENTS:

ATTACHMENT B

DATA REJECTION SUMMARY

Type of Review: Organic Date : September 21, 1999 Case/SAS No. : _____
Site Name: _____ Lab Name: _____
Reviewer"s Initials : _____ Number of Samples: _____

Analytes Rejected Due To Exceeding Review Criteria For: Number of Compounds /Number of Fractions (Samples)

	Labeled Standards	Holding Times	Calibration	Contamination	ID	Internal Standard	Other	Total # Samples	Total # REJECTED/ Total Analytes in samples Percent		
Dioxin (17)	0	0	0	0	0	0	0	0	0	0	??

Analytes Estimated Due To Exceeding Review Criteria For: Number of Compounds /Number of Fractions (Samples)

	Labeled Standards	Holding Times	Calibration	Contamination	ID (RT)	Internal Standard	Other	Total # Samples	Total # ESTIMATED/ Total Analytes in samples Percent		
Dioxin (17)	0	0	0	0	0	0	0	0	0	0	??

Note: Asterisk (*) indicates additional Exceedances of Review Criteria